Central Valley
Regional Water Quality Control Board
Public Workshop on the Development of
a Basin Plan Amendment for the Control
of Resticide Discharges



#### Introduction

- Joe Karkoski, Chief, Pesticide TMDL Unit
- Zhimin (Jamie) Lu, Ph.D., Water Resources Control Engineer
- Paul Hann, Environmental Scientist
- Petra Lee, Environmental Scientist

2

# Meeting Agenda

- Introduction/Agenda Review
- Background
- Current Status
  - -Risk Assessment Report
  - –Aquatic Life Use Assessment Report
  - -Monitoring

3			

# Meeting Agenda

- Water Quality Criteria
  - -Background
  - -Data Selection and Evaluation
  - -Criteria Derivation
  - -Chlorpyrifos Criteria
- Next Steps

4

#### Previous Regional Board Efforts

- Diazinon/chlorpyrifos had been identified as significant water quality problems
- Basin Plan Amendments adopted for:
  - Sacramento/Feather Rivers
  - Sacramento urban creeks
  - San Joaquin River
  - Delta (pending State Board/EPA approval)

5

#### Lessons Learned

- Key regulatory provisions are similar for each water body
- Alternatives to the pesticides we focus on may cause water quality problems
- Close communication and collaboration w/ DPR & Ag Commissioners was important
- Pesticide manufacturers can play positive role to protect water quality through label changes and provide scientific/technical information

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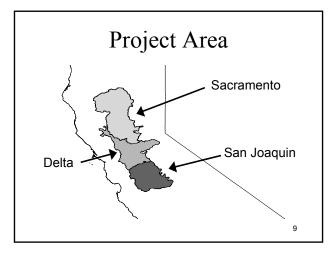
#### Comments from Public

- Tributary streams are important
- Potential impacts of alternative pesticides should be evaluated
- Additive or synergistic impacts should be considered
- Numeric water quality objectives should be established
- Consider alternatives to US EPA's method for deriving water quality criteria

7

# Proposed Scope of Basin Plan Amendment

- Geographic scope Sacramento and San Joaquin watersheds
- Waterways Natural streams below major reservoirs that could receive pesticide discharge from urban or agricultural areas
- Pesticides to address currently registered on 303(d) list plus an additional 3-5 identified as potentially "high" risk to aquatic life



# Proposed Scope of Basin Plan Amendment

- Natural streams not identified in Basin Plan – review appropriate aquatic life beneficial uses
- Establish numeric water quality objectives for pesticides that impact water column
- Establish narrative sediment quality objectives and policies for determining compliance

10

# Proposed Scope of Basin Plan Amendment

- Establish "Total Maximum Daily Loads" and any other regulatory provisions to ensure attainment of objectives
  - Provisions will consider how to effectively implement through existing NPDES and Irrigated Lands programs
- Consider and estimate cost of any proposed regulations
- Establish any necessary monitoring provisions

11

12

#### Workshops / Outreach

- October 2006 Status Update
- May 2006 Status Update
  - Water quality criteria Phase 1 Report
- February 2006 CEQA Scoping Meetings

#### **Current Status**

- Sediment Quality Objectives
  - -Gathering background information
  - Attending Bay Protection ToxicHot Spots meetings

13

15

RELATIVE RISK EVALUATION FOR
PESTICIDES
USED IN
THE SACRAMENTO - SAN JOAQIN
RIVER AREA



Zhimin (Jamie) Lu

# Objectives

- Evaluate the relative risks of selected target pesticides that may impact
  - Surface water quality
  - Sediment quality
- Identify pesticides for additional follow-up

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# **Project Area**

- Three sub-areas:
  - Lower Sacramento River Watershed (SacR): 5,869,138 acres.
  - Lowe San Joaquin River watershed (SJR): 3,234,447 acres.
  - Legal Delta and the tributaries (Delta):
     3,359,003 acres

16

#### **Data Sources**

- Pesticides use data (DPR PUR database)
- Toxicity data (US EPA)
- Physical/Chemical data (ARS)
- Pesticides concentration data (DPR SWDB database)

17

# Methodology

- Initial list
  - For Ag use: Top 30 pesticides in high annual use in terms of pounds and acreage
  - For non-Ag use: Top 60 pesticides in high annual use in terms of pounds only
- Target list
  - Pesticides ranked as very high or high toxicity

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# Define Agricultural and Non-agricultural uses

(DPR PUR definition)

- Agricultural use: crops and nurseries
- Non-agricultural use:
   Commercial uses on structures and landscaping, and public health

# Total pesticides used in the watershed

- Pesticides used in Ag:
  - Three sub-area: SacR, SJR, and Delta
- Pesticides used in Non-Ag:
  - Butte County
  - Sacramento County
  - San Joaquin County
  - Stanislaus County

20

#### Introduction of Terms

- LC50/EC50 values: Lethal Concentration to 50% of tested population (LC50); Effective Concentration at 50% of tested population (EC50)
- Water Solubility: the maximum amount of the pesticide that will dissolve in one liter of water
- Soil absorption coefficient, Koc: the ratio of the mass of pesticide adsorbed per unit mass of soil to the mass of the pesticide remaining in solution at equilibrium
- Half-life in soil: time required for half of the pesticide to degrade in soil

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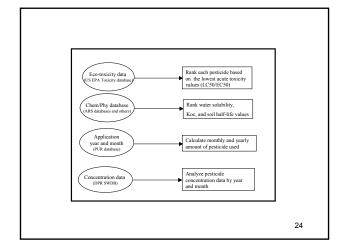
# Criteria for Risk Ranking

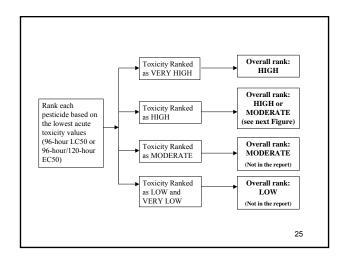
Parameter	Very high	High	Moderate	Low	Very low
Toxicity (96 hour LC50 or EC50)	<1 μg/L	1 to 99 μg/L	100 μg/L to 999 μg/L	1 mg/L to 99 mg/L	>100 mg/L
Log(water solubility (mg/L))	> 3	2.001 to 3	1 to 2	≥0 and <1	<0 (water solubility less than 10)
Koc	>10,000	1,000 to 9,999	100 to 999	10 to 99	<10
Half-life in soils (day)	>1,000	101 to 1,000	31 to 100	10 to 30	<10

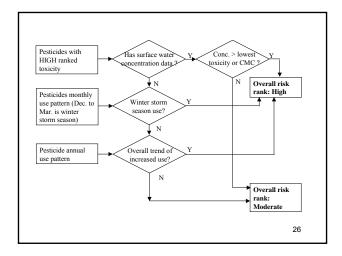
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# Herbicides

ChemName	Lowest Toxicity Value (ug/L)	Test Time and Range	EC50 Ranges	96hr LC50 Range (ug/L)
(S)-METOLACHLOR	8	120 hr(48 to 120hr)	8 to 10	1,410 to 11,900
BROMACIL	6.8	120 hr	6.8 to 69.9	32,000 to 180,000
DIURON	2.4	96hr (48 to 260 hr)	2.4 to 8,400	160 to 300,000
HEXAZINONE	6.8	120hr (48 hr to 21D)	6.8 to 151,600	78,000 to 1,000,000
NORFLURAZON	13	120hr(120hr to 14D)	13 to 86	5,530 to 16,300
OXYFLUORFEN	0.29	96hr (48 to 240 hr)	0.29 to 1,500	31.7 to 1,000,000
PARAQUAT DICHLORIDE	0.55	96hr (48hr to 14D)	0.55 to 50,000	11,000 to 156,000
PENDIMETHALIN	5.2	120hr (120hr to 14D)	5.2 to 174	138 to 90,400
PROPANIL	16	120hr (120 hr to14D)	16 to 110	400 to 16,000
SIMAZINE	36	120hr (48 hr to 14D)	36 to 5,000	3,000 to 1,000,000
TRIFLURALIN	8.4	96hr	15.4 to 5.000	8.4 to 2.800







#### Results

- Evaluated 36 pesticides
  - Overall risk ranked as High:26 pesticides
  - Overall risk ranked as moderate:10 pesticides

# Overall Rank: High Pyrethroids

Ag Us e	Non- Ag Us e	ChemName	Rank of Water solubility	Rank of Koc	Rank of half-life	Rank of Sediment
	y	CYPERMETHRIN	Very Low	Very High	Low	Potential
	у	BIFENTHRIN	Very Low	Very High	Low	Potential
у	у	CYFLUTHRIN	Very Low	Very High	Low	Potential
	у	DELTAMETHRIN	Very Low	High	Low	Potential
у		ESFENVALERATE	Very Low	High	Moderate	Potential
у		LAMBDA-CYHALOTHRIN	Very Low	High	Moderate	Potential
у	у	PERMETHRIN	Very Low	Very High	Moderate	Potential

28

# Pyrethroid Insecticides

- ■Low Water solubility (0.0002 to 0.1 mg/L)
- High Koc (2,341 to 237,000)
- High toxicity to aquatic organisms (0.0017 to 0.07 µg/L)

29

## DPR re-evaluation

- Pyrethroid insecticides
- <a href="http://www.cdpr.ca.gov/docs/sw/ca2006-13.pdf">http://www.cdpr.ca.gov/docs/sw/ca2006-13.pdf</a>

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# Overall Rank: High -Very high toxicity

Ag Us e	Non- Ag Us e	ChemName	Pesticides Type	Rank of Water solubility	Rank of Koc	Rank of half-life	Rank of Sediment
y	y	OXYFLUORFEN	Herbicide	Very Low	Very High	Moderate	Potentia1
У		PARAQUAT DICHLORIDE	Herbicide	Very high	Very High	Very High	Potential
У		ABAMECTIN	Insecticide	Low	High	Low	Potentia1
У	у	CHLORPYRIFOS	Insecticide	Low	High	Moderate	Potential
У	у	DIAZINON	Insecticide	Moderate	High	Very Low	Potential
	у	FIPRONIL	Insecticide	Moderate	Moderate	High	Possible
	y	MALATHION	Insecticide	High	High	Very Low	Potentia1

31

# Overall Rank: High

-High toxicity

Ag Us e	Non- Ag Us e	ChemName	Pesticides Type	Rank of Water solubility	Rank of Koc	Rank of half-life	Rank of Sediment
у		(S)-METOLACHLOR	Herbicide	High	Moderate	Moderate	Possible
y	у	CHLOROTHALONIL	Fungicide	Very Low	High	Moderate	Potential
y	у	DIURON	Herbicide	Moderate	Moderate	Moderate	Possible
v	v	IMIDACLOPRID	Insecticide	High	Moderate	High	Possible
y	y	MANCOZEB	Fungicide	Low	High	Moderate	Potential
y		MANEB	Fungicide	Low	Moderate	Moderate	Possible
y		PROPANIL	Herbicide	High	Moderate	Very Low	Possible
y		PROPARGITE	Insecticide	Very Low	High	Moderate	Potential
y		PYRACLOSTROBIN	Fungicide	Moderate	Low	High	Unlikely
y	у	SIMAZINE	Herbicide	Low	Moderate	Moderate	Possible
v	v	TRIFLURALIN	Herbicide	Very Low	High	Moderate	Potential
v		ZIRAM	Fungicide	Moderate	Moderate	Moderate	Possible

32

# Overall Rank: Moderate

Ag Us e	Non- Ag Use	ChemName	Pesticides Type	Rank of Water solubility	Rank of Koc	Rank of half-life	Rank of Sediment
	у	BROMACIL	Herbicide	High	Low	High	Unlikely
у		CARBARYL	Insecticide	High	Moderate	Low	Possible
y	у	CAPTAN	Fungicide	Low	Moderate	Very Low	Possible
у		INDOXACARB	Insecticide	Low	High	Moderate	Potential
	у	NALED	Insecticide	Low	Moderate	Very Low	Possible
	у	NORFLURAZON	Herbicide	Moderate	Moderate	High	Possible
y		DIMETHOATE	Insecticide	Very high	Low	Very Low	Unlike ly
y		HEXAZINONE	Herbicide	Very high	Low	Moderate	Unlikely
у		METHOMYL	Insecticide	Very high	Low	Low	Unlikely
	v	PENDIMETHALIN	Herbicide	Very Low	Very High	High	Potential

## Results

- Sediment risk
- Evaluated 36 pesticides based on their Koc Rank

-Potential: 19 pesticides-Possible:12 pesticides-Unlikely: 5 pesticides

34

## Sediment Risk: Potential

Ag Use	No n-Ag Us e	ChemName	Soil Koc	Rank of Koc	Rank of Sediment
y		ABAMECTIN	5000	High	Potential
	у	BIFENTHRIN	2.37E+05	Very High	Potential
у	у	CHLOROTHALONIL	5000	High	Potential
у	у	CHLORPYRIFOS	9930	High	Potential
у	у	CYFLUTHRIN	31,000	Very High	Potential
	у	CYPERMETHRIN	6.10E+04	Very High	Potential
	у	DELTAMETHRIN	6291	High	Potential
у	у	DIAZINON	1520	High	Potential
v		ESFENVALERATE	5273	High	Potential
у		INDOXACARB	9,400	High	Potential
y		LAMBDA-CYHALOTHRIN	2341	High	Potential
	у	MALATHION	1200	High	Potential
у	у	MANCOZEB	6000	High	Potential
у	у	OXYFLUORFEN	100,000	Very High	Potential
у		PARAQUAT DICHLORIDE	162,000	Very High	Potential
	y	PENDIMETHALIN	13,400	Very High	Potential
v	v	PERMETHRIN	39,300	Very High	Potential
v		PROPARGITE	5578		Potential
v	y	TRIFLURALIN	7200	High	Potential

# Sediment Risk: Possible

Ag Use	Non-Ag Use	ChemName	Soil Koc	Rank of Koc	Rank of Sediment
у		(S)-METOLACHLOR	185	Moderate	Possible
y	у	CAPTAN	151	Moderate	Possible
y		CARBARYL	288	Moderate	Possible
y	у	DIURON	477	Moderate	Possible
	у	FIPRONIL	749	Moderate	Possible
y	у	IMIDACLOPRID	262	Moderate	Possible
y		MANEB	240	Moderate	Possible
	у	NALED	157	Moderate	Possible
	у	NORFLURAZON	353	Moderate	Possible
у		PROPANIL	400	Moderate	Possible
y	у	SIMAZINE	140	Moderate	Possible
V		ZIRAM	400	Moderate	Possible

# Sediment Risk: Unlikely

Ag Us e	Non-Ag Us e	ChemName	Soil Koc	Rank of Koc	Rank of Sediment
	У	BROMACIL	14	Low	Unlikely
у		DIMETHOATE	20	Low	Unlikely
y		HEXAZINONE	54	Low	Unlikely
у		METHOMYL	32	Low	Unlikely
у		PYRACLOSTROBIN	93	Low	Unlikely

37

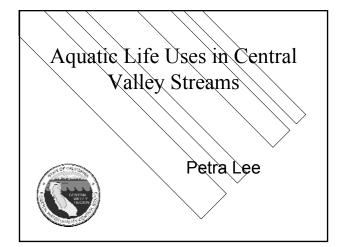
# Summary

- Target pesticides include relatively new and old pesticides for both Ag and Non-Ag applications
- The ranking of the relative risk can be used for further study (e.g., water quality criteria, monitoring)

38

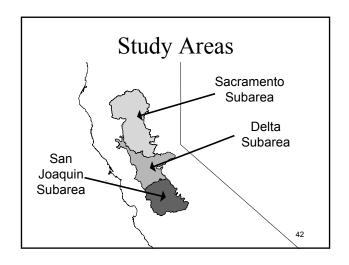
# Questions?

Please submit comments to Zhimin (Jamie) Lu zlu@waterboards.ca.gov (916)464-4830



# Purpose

- Describe Aquatic Life Uses (ALU) within natural streams of Central Valley Pesticide Basin Plan Amendment Project Area
  - Compile aquatic life use information providing evidence that ALUs exist
  - List natural streams by name and location (700-800)
- Water Quality Criteria developed could be applied to streams with Aquatic Life Beneficial Uses



#### Beneficial Uses – Aquatic Life Uses

- Municipal and Domestic Supply
- Agricultural Supply
- Ground Water Recharge
- Navigation
- Etc...

- Warm Freshwater Habitat
- Cold Freshwater Habitat
- Migration of Aquatic Organisms
- Freshwater Replenishment Spawning, Reproduction, and/or Early Development

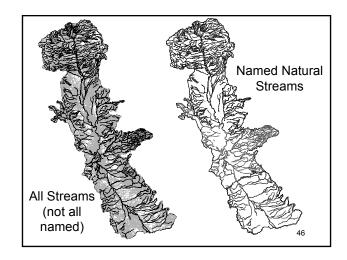
"Uses of water that support [warm or cold] water ecosystems including, but not limited to, preservation or enhancement of aquatic habitats, vegetation, fish, wildlife, including invertebrates."

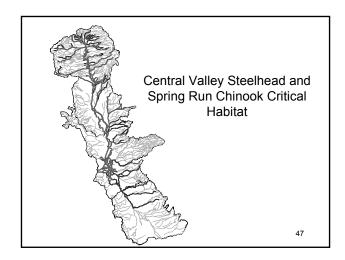
**Data Compilation** 

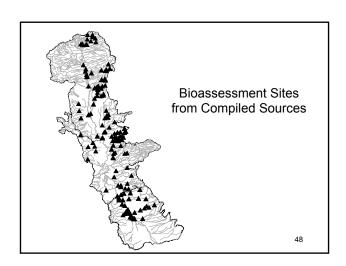
- Bioassessment data
  - -USGS, DFG, DPR, SWAMP, etc.
- Two pieces of information from bioassessment
  - -Location
  - -Was there aquatic life?

# **Data Compilation**

- Critical Habitat Data (NOAA)
  - -Central Valley Steelhead
  - -Central Valley Spring-Run Chinook
- Mapping Database/GIS Layer to obtain stream names





#### **Tentative Conclusions**

- All sites in all reports had aquatic life
- Suggests that 1 or more Aquatic Life Uses exist in all Project Area natural streams

49

#### The Future

- Finish informal external peer review
- Release public draft
- Release final draft

50

#### **More Information:**

http://www.waterboards.ca.gov/centralvalley/programs/tmdl/pest-basinplan-amend/index.html

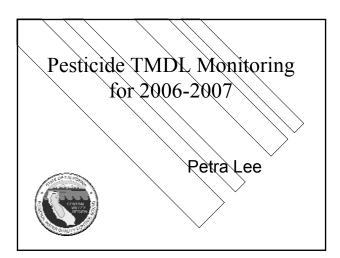
#### **Contact Information:**

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# Questions?



## Overview

- Introduction
- Briefly discuss results for 2006
  - Ag monitoring
    - » Storm
    - » Irrigation
- Plans for 2007
  - Ag monitoring (irrigation only)
  - Urban monitoring

# Overview of Monitoring

- Based initially on Relative Risk Assessment report 2006
- Department of Pesticide Regulation's Pesticide Use Report
- PUR database to determine months of highest use
- Placed monitoring site downstream of high use areas

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#### Coordination

- Within Central Valley Regional Board
  - Irrigated Lands Program
  - Stormwater Program
- Department of Pesticide Regulation
- Coalition groups
- SWAMP

56

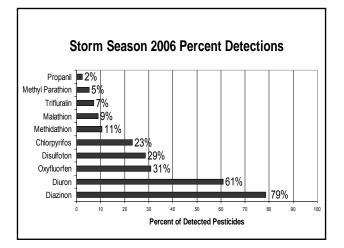
# 2006 Pesticide Analytes

Pesticide Group	Target Pesticides
OP's	Diazinon, chlorpyrifos, azinphos methyl, malathion, methidathion, methyl parathion
Carbamates	Diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl
Herbicides	Propanil, propargite, oxyfluorfen, trifluralin
Other	Paraquat dichloride 57

# 2006 Monitoring Sites

- Nine (9) sites in Sacramento River Basin
- Four (4) sites within Eastern Delta Tributaries
- Five (5) sites within San Joaquin River Basin

58



# Storm Season 2006 Highlights

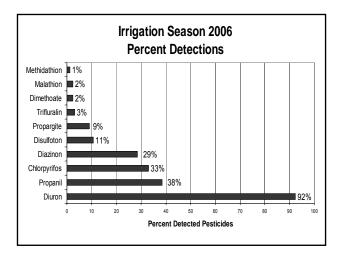
#### ■ Diazinon 79% of samples

- Several samples above 0.100 ug/L chronic criterion
- All samples at Live Oak Slough at Nuestro Road & Morrison Slough at Luckehe Road exceeded chronic criterion
- Almost all samples exceeded chronic criterion at Pixley Slough at Ham Ln
- Detection at every single site


# Storm Season 2006 Highlights continued

- Diuron 61% detection
  - -Herbicide
- Chlorpyrifos, disulfoton, oxyfluorfen 20-30% detection
  - Chlorpyrifos above 0.015 ug/L chronic criterion 4 times, at two sites

61



# Irrigation Season 2006 Highlights

- Diuron 92% detected
  - -Herbicide
- Propanil 38% detected
  - -Rice pesticide

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# Irrigation Season 2006 Highlights continued

- Diazinon 29% detection
  - 0 exceedances of 0.100 ug/L chronic criterion
  - Higher concentrations up north
- Chlorpyrifos 33% detection
  - 6 exceedances of 0.015 ug/L chronic criterion
  - Higher concentrations down south

64

# Changes for 2007!

- Agricultural monitoring
  - Herbicides only (oxyfluorfen, trifluralin, propargite, propanil)
  - Changed sites accordingly
  - No paraquat dichloride
- Added 3 urban sites
  - Fipronil
  - Triazines
- No early 2007 storm season (contract problems)

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#### 2006-7 Similarities

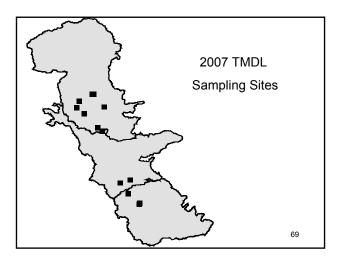
- ■UC Davis sampling using SWAMP methods
  - -SWAMP comparable
- Same analyses
  - -Added fipronil & triazines
- Dept of Fish & Game lab doing analyses

# 2007 Pesticide Analysis

Specific Analytes
Propanil, propargite, oxyfluorfen, trifluralin
Diuron, carbofuran, carbaryl, methiocarb, aldicarb, captan, linuron, methomyl
Diazinon, chlorpyrifos, azinphos methyl, malathion, methidathion, methyl parathion
Ametryn, atraton, atrazine, prometon, prometryn, propazine, secumeton, simazine, simetryn, terbuthylazine, terbutryn
Fipronil

# 2007 Pesticide TMDL Monitoring Sites

- Eight (8) sites within Sacramento River Basin
- Four (4) sites within Eastern Delta Tributaries & San Joaquin River Basin
- Three (3) urban creek sites
  - Two (2) in Sacramento
  - One (1) in Stockton
- San Joaquin River at Crow's Landing (OP's)



#### **More Information:**

<u>http://www.waterboards.ca.gov/centralvalley/programs/tmdl/pest-basinplan-amend/index.html</u>

#### **Contact Information:**

#### Petra Lee

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70

# Questions?

71

Central Valley
Regional Water Quality Control Board

Water Quality Criteria Method Development



Paul Hann – Environmental Scientist phann@waterboards.ca.gov

Joe Karkoski – Senior Water Resources Engineer ikarkoski@waterboards.ca/gov

#### Previous Regional Board Efforts

- Diazinon/chlorpyrifos had been identified as significant water quality problems
- Basin Plan Amendments adopted for:
  - Sacramento/Feather Rivers (Revision Pending)
  - Sacramento urban creeks
  - San Joaquin River
  - Delta

73

#### **Past Public Comments**

- Potential impacts of alternative pesticides should be evaluated
- Additive or synergistic impacts should be considered
- Numeric water quality objectives should be established
- Consider alternatives to US EPA's method for deriving water quality criteria

74

## Criteria, Not Objective

- Water Quality Criteria A numeric level above which beneficial uses may be impaired
- Water Quality Objective Limits on constituents established for the protection of beneficial uses of water or the prevention of nuisance
  - Narrative objectives are expressed in qualitative terms
  - Numeric objectives include a specific concentration
  - Water Quality Objectives consider protection of beneficial uses and other values

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#### Potential Uses of Criteria

- Establishment of Water Quality Objectives
  - Would require additional evaluation consistent with Porter Cologne.
- Interpretation of Narrative Objective
  - 303(d) List
  - NPDES & Irrigated Lands Waiver Programs
- DPR during registration / re-evaluation?

76

## Background

- Past water quality criteria have been based on the 1985 EPA Guideline for Derivation of Numeric Water Quality Criteria
- Current EPA Method has been used successfully for many years
- Newer methods have become available and merit review
- Regional Board is looking for a method that can handle limited data sets
  - Current alternative is 1/10th of the lowest LC50

77

78

## Research Study Overview

- Researchers from UC Davis are under contract to assist with the review of Water Quality Objectives
- Purpose: Identify/develop a method(s) for deriving numerical water quality criteria that are protective of aquatic life and could be used as the basis for pesticide water quality objectives in the Central Valley

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## Research Study Objectives

- Ensure that criteria are scientifically defensible
- Incorporate current scientific thinking
- Include methodology for establishing numeric criteria for pesticides having limited data
- Provide for comprehensive review of multiple pesticides
  - Diazinon and chlorpyrifos to begin with
  - At least 3 additional pesticides this year
  - Possibly additional pesticides next year

79

#### Changes in Research Team

- Project Researcher recently left UC Davis to work with US EPA
- New researchers have been identified and are familiarizing themselves with the project
- During the transition, Central Valley Water Board Staff will present the method.
- Staff is still reviewing the methodology and is soliciting comments from interested stakeholders.

80

81

# Summary of Method Elements

- Guidance on collection and evaluation of raw data
- Alternatives for various sizes of datasets
- Ability to address acute and chronic exposures
- Ability to adjust criteria based on environmental factors
- Method elements are selected or based upon elements from other established methods.

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#### Collection of Raw Data

- Required Data
  - Physical-Chemical
  - Ecotoxicity
  - Human Health data
- Includes a table of recommended places to find data
  - 15 different handbooks, journals, review articles, etc.
  - 25 different electronic sources including online databases and software tools
- Refer to Tables 3.1, 3.2 and 3.3 in supplemental handouts

82

#### Collection of Raw Data

- Provides means to fill chronic data gaps with extrapolation techniques
  - Extrapolation technique to estimate chronic toxicity from acute toxicity
  - Adopts U.S. EPA ACE program
  - Requires data that includes exposure concentrations and measurement of effects at multiple time points

83

#### Collection of Raw Data

- Provides guidance on how to consider nontraditional endpoints and data from multispecies studies
  - Nontraditional endpoints may be used if they can be linked to effects on survival growth and reproduction (Species Specific)
  - Multi-species data are used for comparison to derived criteria and can be used as justification for adjustment of a final criterion.

#### Evaluation of Data

- Physical-Chemical parameters must be performed by one of the approved methods. – See Table 3.4-3.5 (exception for some established references)
- Only toxicity studies with acceptable relevance and reliability scores can be used
  - Several Tables are provided to determine relevance and reliability scores
  - Relevance The extent to which a test is appropriate for a particular hazard (Score must be >70)
  - Reliability inherent quality of a test relating to test methodology and the way that the performance and results of the test are described.

85

#### Evaluation of Data

- Reliability is evaluated as the combination of Documentation and Acceptability (Tables 3.7-3.10)
  - Documentation Was the study effectively documented
  - Acceptability Do the lab procedures meet minimum requirements
- Documentation and Acceptability Scores are averaged and compared to Table 3.11
  - Only data rated Relevant and Reliable may be used for criteria derivation.
  - Less relevant/reliable (LL, LR, RL) data can be used for supporting data.

86

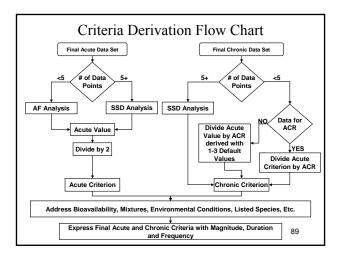
#### **Data Reduction**

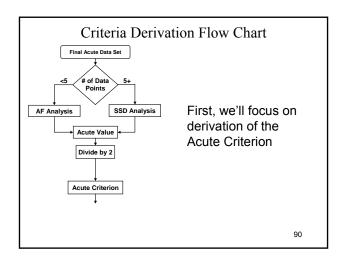
- Data are reduced such that each species has one representative data point in the final data set.
  - SMAV Species (geometric) Mean Acute Value Based on  $LC_{\rm 50}$
  - SMCV Species (geometric) Mean Chronic
     Value Based on Maximum Allowable Toxicant
     Concentration (MATC)
  - Use most sensitive life stage and endpoint for each species
- Final data set is collection of SMAV/SMCV

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## **Data Reduction**

- Additional Procedures provided to account for:
  - Conversion of NOEL/LOEL to MATC Geometric mean of NOEL and LOEL
  - If no toxicity values were reported, but raw data are available, they can be calculated using an appropriate statistical technique
  - Multi-modal data if data is multimodal, divide the data into subsets and use more sensitive subset.
  - Test for Outliers If distribution cannot be fit due to data outlier (outlier test provided), remove the datapoint, recognizing that criteria may need to be adjusted later.





## Size of Final Data Set

- To use the Species Sensitivity Distribution procedure (SSD), the final data sets must include at least 5 SMAV with representatives of all of the following:
  - Family Salmonidae
  - Warm water fish
  - Planktonic crustacean, of which must be in family Daphniida in the genus Ceriodaphnia, Daphnia, or Simpocephalus
  - Benthic Crustacean
  - Insect (for non-herbicide), or alga or vascular plant (for herbicides)
- Assessment Factor Method is used for other datasets

91

## SSD Analysis

- Statistical Method
- SMAV are plotted and curve fit using a Burr III distribution
- Recommended Acute Value is the median estimate of the 5<sup>th</sup> percentile value
  - Procedures allows for other protection and confidence levels
- Note: Acute Value ≠ Acute Criterion

92

# Justification of 5<sup>th</sup> Percentile and Conversion to Acute Criterion

- SSD is a statistical technique
  - The lower end tail extends indefinitely there is no 0<sup>th</sup> percentile (i.e. no potential for adverse impact) – We have to choose some threshold
  - The further out onto the tail, the greater the uncertainty
  - 5<sup>th</sup> Percentile represents a balance between protection and certainty
  - Criteria established using a 5<sup>th</sup> percentile level within the methodology generates criteria that correspond well to NOEL seen in experimental stream studies.
- Because the Acute Value is based on LC<sub>50</sub> data, an additional safety factor of 2 is applied

94

#### **Assessment Factors**

Acute Value = Lowest Value In Data Set
Assessment Factor

- Used where data requirements for SSD cannot be met.
- Size of the Assessment Factor is dependent on the number of SMAV available
  - Ranges from 5.1 (4 SMAV) to 570 (1 SMAV)
  - DPR Requires at least 3 Toxicity Tests, so AF based on 1 or 2 data points should not occur in practice
- As with SSD technique, an additional safety factor of 2 is applied in converting the acute value to an acute criterion in order to compensate for using LC<sub>50</sub> data

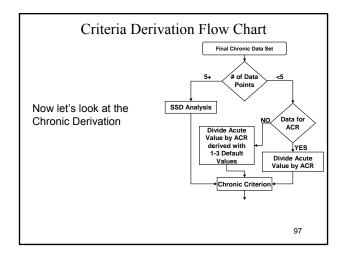
95

#### **Assessment Factors**

- 5 Data points = Use SSD Method
- 4 Data points = 5.1
- 3 Data points = 7.8

Minimum DPR Requirement

- 2 Data points = 36
- 1 Data point = 570 (includes safety factor to protect against cases where Daphnids are among most tolerant species.



#### Size of Final Data Set

- SSD is used for data sets with 5 or more SMCV
- Procedure is equivalent to Acute SSD, except:
  - SMCV are used
  - SMCV are based on MATC
  - No Safety Factor is applied to convert the Chronic Value to a Chronic Criterion
- Acute to Chronic Ratio procedure is used for other datasets

98

#### Acute to Chronic Ratio

 $Chronic Criterion = \frac{Acute Value}{ACR}$ 

- Used with data sets having fewer than 5 SMCV
- ACR is the ratio of the acute values to available chronic values
- Default ACR's can be used if there is not enough data to calculate a single-chemical ACR
  - Use 1-3 Default ACR Values (substitute until 3 data points are available
  - The Default ACR is based on the 80<sup>th</sup> percentile of pesticide ACRs reported in USEPA and CDFG criteria
  - Default ACRs are intended to be updated as new data becomes available

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# Once the acute and chronic criteria are derived, they are reviewed to address physical and environmental factors Acute Criterion Chronic Criteria with Magnitude, Duration and Frequency

#### Potential Adjustments

- Mixtures Method provides procedure for additivity and non-additive synergy or antagonism.
  - Additivity Method Allows compliance with criteria to be determined using either the Toxic Unit approach (current method used in Basin Plan) or the Relative Potency Factor (Recommended by peer reviewer)
  - Synergism and Antagonism Method provides an procedure to assess compliance where valid multi-species interaction coefficients are known.

10

#### Potential Adjustments

- Bioavailability
  - Pesticides may be sorbed onto suspended or dissolved solids or freely dissolved in the water.
  - Method provides procedure to determine compliance with the objective where pesticide may not be bioavailable in one phase
    - » Does not result in change in WQC, simply addresses how to interpret sampling results
    - » Pesticides may be directly measured in each phase or calculated using physical data

## Potential Adjustments

- Temperature, pH and other Effects adopts EPA 1985 procedure to address other water quality effects
- Sensitive/Listed Species Adjust criteria downward if it is higher than a reported value for a sensitive and listed species - Procedure to use surrogate species if no data is available for listed species

## Potential Adjustments

- Bioaccumulation procedure to address potential chronic affects to wildlife and human health through bioaccumulation in fish or other food items. Does not apply to acute criteria
- Ecosystem Studies If toxicity values in multispecies or ecosystem studies are lower than derived criteria, the criteria may be adjusted.
- Harmonization across media Procedure to ensure that water criteria will not result in harmful levels in other media (i.e. soil and air)

#### Comparison to Other Methods

	1/10th LC50	EPA 1985	New Method
Source Evaluation Guidelines	None	Limited	Extensive
List of Sources	None	None	Yes
SSD or AF	AF	SSD	SSD or AF
AF Empirically Based	No	N/A	Yes
Minimum Data Required	1	8	1 (AF) or 5 (SSD)
All Data Used	No	Not Directly	Yes
SSD Cutoff	N/A	5 <sup>th</sup> Percentile	5 <sup>th</sup> Percentile
SSD Fit Method	N/A	Log Triangular	Burr III Family

106

## Test Case - Chlorpyrifos

- Acute final data set contained 17 SMAV
  - SSD procedure used 11.5 ng/L (0.0115  $\mu$ g/L)
  - AF procedure used for comparison ranged from 0.03 ng/L to 3.4 ng/L depending on how many and which SMAV were assumed to be available.
- Chronic final data set contained 3 SMCV
  - ACR Procedure used 10.5 ng/L (0.0105 μg/L)

107

#### Test Case - Chlorpyrifos

- Environmental Factors Evidence was found for temperature dependency, but insufficient data was found to quantify the relationship. No other environmental factors suggest that adjustments are recommended.
- Bioavailability Studies of chlorpyrifos bioavailability were few and indicated that bioavailability of chlorpyrifos is not predictable without site specific, species specific data.

108			
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#### Test Case - Chlorpyrifos

#### ■ Mixtures

- Recommended considering simple additivity with other organophosphates.
- Evidence of non-additive (synergistic) effects with triazine herbicides. A quantitative relationship was identified for chlorpyrifos in the presence of atrazine.
- Evidence of non-additive (antagonistic) effects with PBO, but a quantitative relationship could not be established

109

#### Test Case – Chlorpyrifos

■ Sensitive and Listed Species – Derived criteria are below the lowest acute and chronic values in the dataset, so they should be adequately protective based on current available data. Criteria was compared to available data for listed species and determined to be protective, with the caveat that the dataset is lacking suitable data for the effects of chlorpyrifos on federally endangered cladocerans or insects.

110

#### Test Case – Chlorpyrifos

- Bioaccumulation The proposed criteria should not result in unacceptable levels of bioaccumulation
- Ecosystem and Other Studies The proposed criteria should be protective of ecosystem.
- Harmonization across media fugacity and partitioning models indicate that the proposed criteria should not cause problems in other environmental compartments.

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## Test Case - Chlorpyrifos

Comparison to Other Criteria (ng/L)					
Criteria	Acute	Chronic			
USEPA 1986	83	41			
Lowest Toxicity Datum	35	40			
Basin Plan WQO	25	15			
US EPA 1985 Using Same Dataset as New Method	17	15			
New Method	11.5	10.5			

112

#### **Comment Solicitation**

- Staff is still reviewing the method and application to chlorpyrifos.
- Staff is not yet endorsing the method and application
- Staff is soliciting comments from interested stakeholders

113

# WQC Method Development - Next Steps

- Written Comments on the Phase I and Phase II reports received by May 18, 2007 will be responded to as part of the Phase III report.
- Phase III (2007) will consist of
  - Derivation of Diazinon Criteria
  - Comparison of Diazinon and Chlorpyrifos to other methods using the same data set
  - Derivation of at least 3 additional Pesticides
- Possible Phase IV (2008) to derive additional Pesticides

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# **Send Comments**

- By e-mail to <a href="mailto:phann@waterboards.ca.gov">phann@waterboards.ca.gov</a>
- By mail to:

Paul Hann Central Valley Water Board 11020 Sun Center Drive # 200

Rancho Cordova, CA 95670-6114

Public Review Draft Report is Available on the Central Valley Water Board Website at:

http://www.waterboards.ca.gov/centralvalley/programs/tmdl/pest-basinplan-amend/index.html#Criteria

115

Questions?

116

# Next Steps

■ Continue work on technical reports